



Improved catalytic oxidation of cumene by formation of catalytically active species during reaction over NaX zeolite

R. Beauchet, J. Mijoin*, P. Magnoux

Laboratoire de Catalyse en Chimie Organique, Université de Poitiers, CNRS UMR 6503, 40 avenue du Recteur Pineau, 86022 Poitiers, France

ARTICLE INFO

Article history:

Received 5 June 2008

Received in revised form 12 September 2008

Accepted 19 September 2008

Available online 27 September 2008

Keywords:

VOCs

Catalytic oxidation

Active coke

Pore mouth catalysis

ABSTRACT

Catalytic oxidation of isopropylbenzene (cumene, 210 ppm) in wet air was essentially investigated over basic NaX zeolite. Experiments were carried out in presence of water (11,000 ppm) and at a gas hourly space velocity (GHSV) of 18,000 h⁻¹. Over NaX, the cumene showed a catalyst activation phenomenon during the reaction time. Indeed, after 175 min of reaction at 250 °C the conversion of cumene increases from 45% to 100% and the CO₂ yield from 30% to 95% probably because of the formation of active species mainly localized at the cavities apertures of the basic zeolite. Peroxide or peroxy radicals were proposed to be these particular active species.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Due to their polluting effects and to their induced disorders to human health, industrial processes must submit to more and more restrictive emissions norms towards Volatile Organic Compound (VOC). Among all processes, thermal oxidation is the most extended technique used to destroy VOCs. However, high temperatures (above 1000 °C) are required and noxious by-products (NO_x) can be formed during the destruction. Contrary to the thermal method, catalytic oxidation allows to destroy VOCs at lower temperature (200–400 °C) without NO_x formation. This technique enables to work at high gas hourly space velocity and with low VOCs concentrations, which places it as a promising technique to reduce VOCs emissions. A wide range of solids can be used for that purpose that are classically transition metals oxides or noble metal supported catalysts [1,2]. More recently, zeolites were considered as effective alternative to oxide based catalysts for air pollution control [3–15]. Indeed, zeolites, which are generally used as molecular sieve, adsorbent or support can also be used, thanks to their high oxidative properties and to their regenerating capacity, to destroy VOCs emissions.

However, pollutants present in industrial gas flow generally contain hydrocarbons (alkenes, alkanes, aromatics), chlorinated

(dichloromethane, tetrachloroethylene) as well as oxygenated VOCs (ketones, alcohols, esters) and only a few detailed studies on the catalytic combustion of mixtures can be found in the literature [5,16–21].

Some previous studies showed that destruction of VOCs could be influenced by many factors among which we can mention, the deactivation of the catalysts due to coke formation during reaction time [16], the effect of humidity present in wet air [22], the dealumination of the zeolite [23], the cation loss during the reaction [22,24], or the formation of refractory by-products [20]. An interesting observation was made in a previous study in which a promoting effect of isopropanol on the catalytic oxidation of *o*-xylene over zeolites was shown [15]. This promoting effect was certainly due to the formation of an intermediary product (isopropylidimethylbenzene), which is easier to oxidize than *o*-xylene. In order to appreciate the role of this intermediary in the reaction scheme of the mixture oxidation, the oxidation of isopropylbenzene (cumene), a more easy to use analogous compound, had been studied over NaX zeolite, one of the most active catalyst for *o*-xylene/isopropanol mixture oxidation [15].

We show in the present work that over this zeolite, an astonishing increase of the cumene oxidation appears as a function of time. This article is therefore devoted to a best understanding of this phenomenon and deals with the possibility of the formation of active species, which would remain, blocked on zeolite pores during cumene oxidation on NaX.

* Corresponding author. Tel.: +33 5 49 45 39 12; fax: +33 5 49 45 37 79.

E-mail address: jerome.mijoin@univ-poitiers.fr (J. Mijoin).

Table 1

Characterization of catalysts: framework formula, Si/Al ratio and specific surface area, carbon content, number of Brønsted (nB) and Lewis (nL) acid sites able to retain adsorbed pyridine at 150 °C, mesoporous (Meso) and microporous (Micro) volumes determined by nitrogen adsorption isotherm at –196 °C over fresh NaX, fresh HY and after cumene oxidation over NaX at 250 °C for different times on stream.

Zeolites	Formula	Si/Al	Specific surface area (m ² g ^{–1})	%C	nB (μmol g ^{–1})	nL (μmol g ^{–1})	Pore volume (cm ³ g ^{–1})	
							Micro	Meso
NaX	Na ₈₈ Al ₈₈ Si ₁₀₄ O ₃₈₄	1.2	743	–	–	1358 ^a	0.301	0.009
HY	H ₃₂ Al ₃₂ Si ₁₆₀ O ₃₈₄	5	659	–	670	248	0.255	0.068
NaX + cumene 80 min	–	–	–	0.9	16	161	–	–
NaX + cumene 160 min	–	–	–	2.4	21	98	–	–
NaX + cumene 300 min	–	–	437	3.1	38	57	0.170	–

^a Corresponds to Pyridine–Na⁺ interaction.

2. Experimental

NaX (Si/Al = 1.2) and protonic HY zeolite (Si/Al = 5) were supplied by Axens and Zeolyst Corporation, respectively. Acidity of the catalysts was characterized by pyridine adsorption followed by IR spectroscopy (Table 1). This technique needs the catalyst to be pressed (pressure of 3 ton cm^{–2}) in thin wafer (16 mm in diameter and 2 cm² of surface area). The pre-treatment consists in activating in situ the catalyst under airflow (60 mL min^{–1}) during 12 h at 450 °C with a ramp of 2 °C min^{–1}. A different pre-treatment is needed for coked zeolite. Indeed, the catalyst is just put under airflow (60 mL min^{–1}) during 1 h at 150 °C with a ramp of 2 °C min^{–1} and then the wafer is let 2 h under vacuum. The adsorption of pyridine results in the appearance of two characteristic adsorption bands (Fig. 1): PyH⁺ in the case of a protonic zeolite (1545 cm^{–1}), and pyridine bonded to Lewis acid sites, PyL (1454 cm^{–1}). The total amounts of Brønsted and Lewis acid sites accessible to pyridine were quantified by the subtraction between P₁₅₀ spectrum (spectrum of the catalyst after adsorption and desorption at 150 °C of pyridine) and P_∞ one (spectrum of the catalyst before adsorption of pyridine). This technique allows to eliminate the intrinsic absorbance of the solid in the wavelength range studied and also to ignore the influence of pyridine physisorption (below 150 °C). The extinction coefficients of the resulting PyH⁺ and PyL bands, i.e. 1.13 and 1.28 cm μmol^{–1}, respectively, were taken from a previous study [25]. Over NaX zeolite, a band corresponding to pyridine bonded to Na⁺ cations appears at 1444 cm^{–1} [26] (Fig. 1). Although this band is located near the Lewis sites one (1454 cm^{–1}), it is not related to the presence of true Lewis acid sites, and no extinction coefficient is available. Therefore, this band is treated like PyL (with the same

extinction coefficient) to give relative information about the ratio of Na⁺ made inaccessible to pyridine.

IR spectroscopy is also able to give structural information about the sample. Indeed, the shift of the TOT bands (ν_1 near 1050 cm^{–1} and ν_2 near 810 cm^{–1}) is correlated to the framework Al atoms number in the zeolite cell [27–29]. For the FAU type zeolites the following calculations were used:

$$N_{Al} = 0.766(1066.7 - \nu_1)$$

$$N_{Al} = 1.007(832.8 - \nu_2)$$

IR was also used to follow coke nature. In this case, the catalyst is pre-treated under airflow (60 mL min^{–1}) during 1 h at 150 °C with a ramp of 2 °C min^{–1} and then 2 h under vacuum before taking the spectrum.

IR spectra of acetophenone adsorbed over NaX were taken using the same pre-treatment used to characterize acidity of fresh NaX. Then, the cell is opened and a liquid mixture of 1 mL dichloromethane/1 μL acetophenone is deposited drop by drop on the wafer. This step must be achieved as rapidly as possible to minimize water adsorption. After dichloromethane evaporation (5 min), the wafer is replaced in the cell under vacuum. Finally, spectrum is taken at ambient temperature. IR spectra of cumene are obtained using the same method with a 1 mL dichloromethane/1 μL cumene mixture.

Coke nature was also studied by mass spectroscopy. This technique needs the coke to be extracted from the zeolite [30]. Coke extraction is carried out in two steps. First, coke is extracted by dichloromethane with a Soxhlet in order to recover the coke located on catalyst surface and the coke easily removed from the pores of the zeolite sample. Second, the zeolite is mineralized with a 40% HF solution. The coke can be then divided in two fractions: soluble coke that can be extracted by dichloromethane and analysed and insoluble coke composed of very polyaromatic compounds that is not analysable.

Adsorption–desorption isotherms of nitrogen at –196 °C were carried out with a Micromeritics ASAP 2010 apparatus. Micropores volumes were obtained by the *t*-plot method and Dubinin–Radushkevich equation was used to calculate the mesoporosity.

The VOC destruction was carried out in a fixed bed reactor (I.D. = 5 mm, length = 90 cm) at atmospheric pressure and followed as a function of time at constant temperatures, the first point being obtained after 1 min of reaction. The catalyst sample (grain size between 200 and 400 μm; catalyst mass = 0.14 g; catalyst bed height = 1.2 cm) was supported in a small plug of glass wool in a vertical glass tubular reactor. The reactor was inserted into an oven, and the temperature was controlled by a Minicor 42. The temperature was measured by a thermocouple inserted near the catalyst bed. The feed gas (20% O₂ in nitrogen + 1.1% water (relative humidity = 33%)) with 210 ppm of cumene was introduced in the reactor with a total flow rate of 75 mL min^{–1}, which

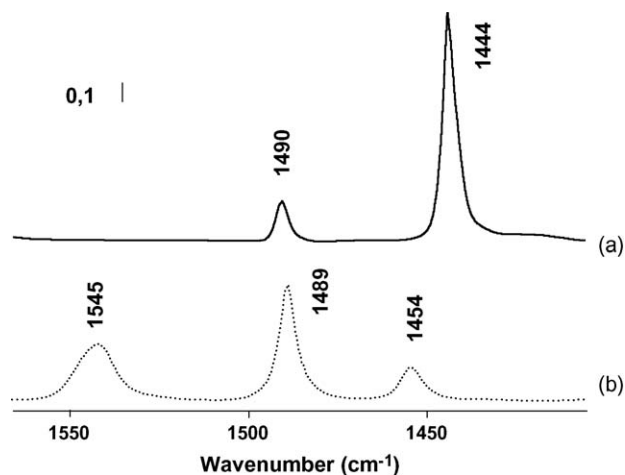


Fig. 1. Difference IR spectrum between IR spectrum measured before and after pyridine adsorption at 150 °C on NaX (a) and HFAU(5) (b).

was controlled by a mass flow controller (Brooks, serie 5850). The desired concentration of VOC was obtained by passing part of the feed gas through a saturator that was kept at the appropriate temperature by means of a cryostatic bath (Hübler). The space velocity (GHSV) was kept constant in all the experiments ($18,000 \text{ h}^{-1}$, calculated at ambient temperature and pressure). An additional by-pass system allowed the analysis of the gas feed without any reaction.

The analytical system consisted in a gas chromatograph (Varian 3400) equipped with a flame ionisation detector for the analysis of the hydrocarbons, and a TCD detector for the analysis of CO_2 . The GC was fitted with a 30 m VF-5 ms capillary column (0.25 mm I.D., 0.25 μm film thickness) for hydrocarbons analysis and with a Porapak Q column for CO_2 quantification. Specific Dräger® tubes (20–500 ppmv range) were also used to detect the eventual production of CO (not found in this work). Cumene conversion, CO_2 yield and instant carbon balance were calculated using the following calculations:

$$\frac{A_0 - A}{A_0} \times 100 = C$$

A_0 is the initial surface area of cumene peak without reaction, A is the surface area of cumene peak during the reaction, C is the conversion of cumene in percent.

$$\frac{A_1}{A_2} \times 100 = C_1$$

A_1 is the surface area of CO_2 peak during the reaction, A_2 is the surface area of CO_2 peak for a total destruction of the cumene (derived from CO_2 calibration), C_1 is the conversion of CO_2 in percent.

$$\frac{[\text{C}_9\text{H}_{12}] \times 9 + [\text{CO}_2]}{[\text{C}_9\text{H}_{12}]_i \times 9} \times 100 = C_b$$

$[\text{C}_9\text{H}_{12}]$ is the cumene concentration during reaction time (from the conversion), $[\text{C}_9\text{H}_{12}]_i$ is the initial cumene concentration, C_b is the carbon balance in percent.

The carbon balance deficit gave us the amount of trapped polyaromatic molecules (coke) but also adsorbed reactant or intermediate molecules especially at the beginning of the reaction. This technique was used in the graphs of this article to continuously follow the “coke” deposition versus time-on-stream. For a more reliable coke measurement, catalyst was recovered after reaction at different time-on-stream and the carbon content deposited on the sample was also measured by total burning at 1020°C under helium and oxygen with a CE Instruments NA 2100 Protein analyser. All the numerical amounts of coke deposits given in this work derive from this method.

3. Results and discussion

3.1. Catalytic oxidation of cumene over NaX zeolite

Catalytic oxidation of cumene was essentially studied over NaX zeolite and Fig. 2 shows at 250°C , as a function of time-on-stream, the conversion of cumene, and its transformation into CO_2 and coke (no by-product even CO was observed in the gas phase). At 250°C , during the first minutes, cumene was totally removed but the deficit in carbon balance seems to show that a great part of cumene was adsorbed or transformed into coke. Then, deactivation occurred and after 80 min of reaction the conversion into cumene was only close to 45%. This conversion was stable during about 100 min. After that, the conversion increased from 45% to 100% during the reaction time while CO_2 yield increases as well (from 30% to 100%). This activation phenomenon was also observed at 280°C (Fig. 3a). However at

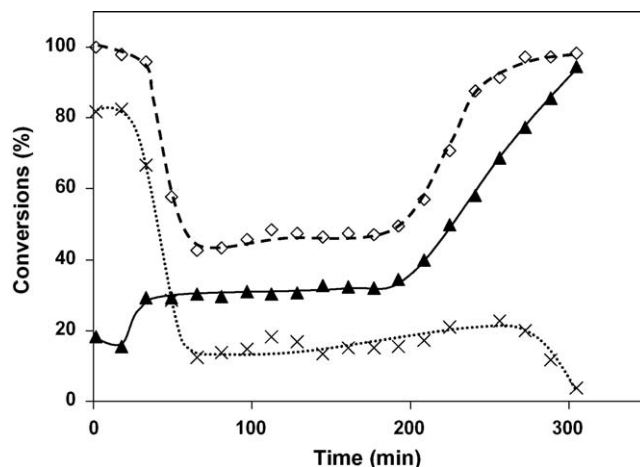


Fig. 2. Catalytic destruction of cumene over NaX at 250°C . Cumene conversion (\diamond), CO_2 yield (\blacktriangle) and coke yield (\times).

280°C , the amount of carbon deposited on the zeolite at the end of reaction was lower (1.8 wt% against 3.1 wt% at 250°C) and the total conversion of cumene into CO_2 was rapidly reached (180 min against more than 300 min at 250°C).

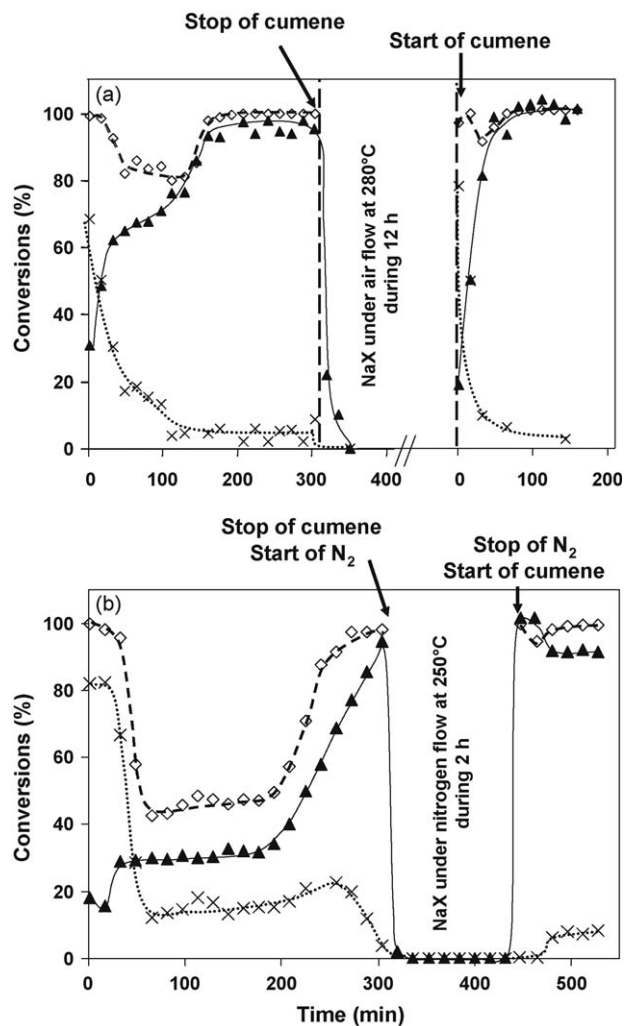


Fig. 3. Catalytic destruction of cumene in 3 steps in wet air over NaX at 280°C (a) and over NaX at 250°C with an intermediate nitrogen flush (b). Cumene conversion (\diamond), CO_2 yield (\blacktriangle) and coke yield (\times).

Some hypotheses for this activating phenomenon can be mentioned:

- (i) Modification of zeolite during the reaction time.
- (ii) Coke combustion.
- (iii) Formation of organic “active coke” species during the reaction.

FTIR pyridine adsorption experiments showed that a very small amount of Brønsted sites appeared (Table 1). This low formation of protonic acid sites results certainly from the exchange of Na⁺ during reaction (presence of steam). However, the loss of Na⁺ cations is very weak and the elemental analysis of NaX before and after reaction confirms the insignificant loss of Na⁺ cations (Na: 10.75% and 10.70% before and after reaction, respectively). Thus, the low formation of protonic acid sites cannot be responsible of the increase of activity of the zeolite during reaction. Indeed, HY zeolite, which exhibits a high acidity (Table 1) was less active since the total destruction of cumene into CO₂ was only observed from 350 °C in the same experimental conditions. It should be noted that on this catalyst, no activation effect was observed whatever the temperatures and the conversions showing that the hypothesis of an eventual exothermic light-off of the catalyst should be invalidated. Indeed, in that case activation should appear on HY too. Moreover, IR study of the TOT bands ($N_{\text{Al}} = 88$ before and after reaction, respectively) and the elemental analysis of NaX showed that the zeolite structure was not significantly modified, which allow to conclude that the first hypothesis is not the best way to explain the activation phenomenon observed.

If activation was due to coke combustion, the amount of carbon deposited on the catalyst should periodically increase and decrease as a function of time and oscillation phenomenon for the CO₂ yield should be observed as it was the case in other studies on NaX zeolite [10,31]. No oscillation was observed and coke content increased continuously with time-on-stream: 0.9, 2.4 and 3.1 wt% after 80, 160 and 300 min of reaction, respectively (Table 1). This shows a constant increase of coke content during reaction and demonstrates that activation is not generated by sudden and massive coke combustion.

To show the effect of coke on cumene oxidation, experiments were carried out in three steps. Fig. 3 shows that coke burning at the end of the reaction could have an influence on conversions if the catalyst is reused for another cumene oxidation. First, cumene oxidation was realized in three steps (Fig. 3a). In the first step, cumene oxidation was carried out at 280 °C during 5 h. Then, cumene flow was stopped and catalyst was maintained under airflow during one night at 280 °C. To finish, cumene flow was restored. These results show that when cumene flow is stopped a part of the coke is oxidized into CO₂. Indeed, at the beginning of the second step we can observe during 45 min a release of CO₂ with no formation of by-product. After 12 h under airflow, oxidation of cumene on the same catalyst always shows activation of cumene conversion and of CO₂ formation but this increase is more rapid. Calculations made with carbon balance indicate that the coke burned at the end of the reaction (0.0008 g) is really close to the quantity of coke deposited (0.0012 g) at the restart of cumene until 100% of CO₂ yield. In addition, the experiment represented by Fig. 3b is also a three steps reaction using N₂ instead of air during the second step. First, the oxidation of cumene was carried out at 250 °C during 5 h. Then, cumene flow was stopped and catalyst was put under nitrogen flow during 2 h. To finish, nitrogen flow was stopped and cumene flow with wet air was restored. With nitrogen, no combustion of coke is observed and when the flow of cumene is restored the conversions are near 100% from the beginning of the third step. This seems to indicate that coke is implicated in the increase of the conversion. The little deactivation

observed at the beginning of the last step could be due to a modification of coke nature during nitrogen treatment at 250 °C during 2 h. Indeed, such an evolution has already been observed over USHY under nitrogen flow in the 250–450 °C temperature range [32]. These experiments show that when coke was oxidized (Fig. 3a) activation was observed again whereas when coke was not destroyed (under N₂, Fig. 3b) no activation occurred and coke was always active even if its structure has evolved during this treatment. In conclusion, coke is active when cumene is oxidized and thus part of the constituent molecules of coke can be considered as active sites towards the oxidation of cumene.

3.2. Structural effect of coke on the catalyst

After 80 min of reaction (0.9 wt% C) catalyst deactivated and about 88% of the Na⁺ sites were made inaccessible to pyridine (Table 1) and only 4% of the Na⁺ remained accessible to pyridine (and certainly to the reactant that has a similar kinetic radius) after 300 min of reaction (3.1 wt% C) whereas the Na content of the catalyst did not significantly vary. This decrease in the Na⁺ Lewis sites accessible to pyridine results from the presence of coke molecules, which block the access of the reactant to the Na⁺ cations. Thus, as the access of usual active sites (Na⁺ cations and associated framework basic oxygen atoms [15]) to the reactant is highly limited, it could be supposed that coke or compounds retained in the zeolite pores acts positively in cumene oxidation. Furthermore, nitrogen (a smaller molecule than pyridine or reactant) adsorption isotherm, showed only a half decrease of the microporous volume during reaction time (0.30 m² g⁻¹ at the beginning against 0.17 m² g⁻¹ at the end of the reaction, Table 1). Therefore, coke molecules essentially restrict the aperture of the zeolite cages letting partially enter nitrogen but not the pyridine (nor the reactant). Consequently, if the reactant is not able to gain access to the microporosity and to the Na⁺ cations, the active coke species are then certainly located near the zeolite supercages apertures.

3.3. Coke nature

After dichloromethane extraction by Soxhlet, a catalyst sample recovered after 300 min of reaction was placed overnight in a drying oven maintained at 90 °C to achieve solvent elimination. Then, an elemental analysis was carried out. The coke content was close to 1.8 wt% against 3.1 wt% before the extraction. It should be noted that no insoluble coke was detected after mineralization by HF and subsequent extraction by dichloromethane. This result shows that 42% of the coke was essentially composed of relatively light molecules, which are soluble in dichloromethane and that the other non extractible molecules were either polyaromatic compounds or aromatic oxygenated molecules soluble in HF solution such as acidic compounds. The soluble coke was analysed by GC–MS and results showed the presence of mainly acetophenone. Except residual cumene, benzaldehyde, phenol, benzoic acid and benzylmethylketone were also observed as well as polyaromatic compounds like diphenylethanedione, 1-[1,1'-biphenyl]-4-yl-ethanone, [1,1'-biphenyl]-4-yl-phenyl-methanone, terphenyl and very reactive polyaromatics like 1,3-diphenyl-2-propen-1-one.

As the main compounds analysed as “coke” were cumene and acetophenone, adsorption of these compounds was carried out over NaX zeolite and samples were characterized by IR spectroscopy after activation at 150 °C under airflow and then under vacuum (Fig. 4). The spectra of cumene adsorbed over NaX show the presence of bands between 1490 and 1430 cm⁻¹ characteristic of the C=C bond of monoaromatics (Fig. 4b). Over NaX impregnated with acetophenone, a large band centred on

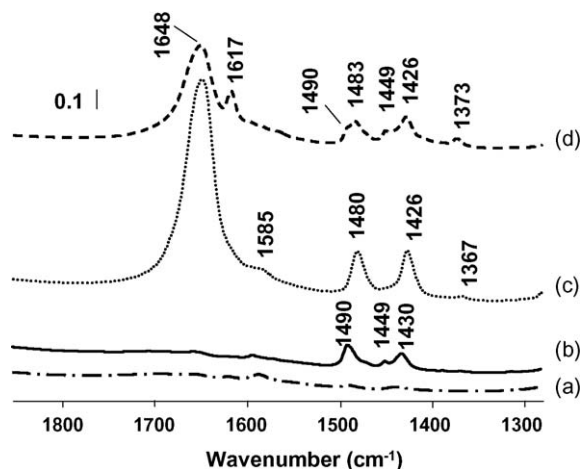


Fig. 4. Spectra of fresh NaX (a), cumene adsorbed on NaX (b), acetophenone adsorbed on NaX (c) and of carbonaceous compounds (coke) retained over NaX zeolite at 250 °C and 80 min of reaction (d).

1648 cm^{-1} characteristic of the C=O vibration of acetophenone is observed (Fig. 4c). Band localized at 1480 and 1426 cm^{-1} ($\nu\text{C}=\text{C}$) is also observed. Fig. 4d shows the spectrum of NaX after 80 min of reaction at 250 °C. It was clear that acetophenone was present in large amount on the sample (large band at 1648 cm^{-1} , bands at 1483 and 1426 cm^{-1}). Band at 1449 cm^{-1} suggests that cumene was also present. However, band at 1617 cm^{-1} was also detected, and is certainly due to the other molecules of coke identified by GC/MS.

Fig. 5 shows the evolution of the IR spectra over NaX as the function of reaction time (80, 160 and 300 min of reaction at 250 °C). These spectra clearly indicate that acetophenone amount decreases drastically during reaction (according to the surface area of the 1648 cm^{-1} C=O band). In fact, we can see by deconvolution that the surface area of the C=O band linked to the presence of acetophenone decreases of about 90% between 80 and 300 min of reaction (surface of the C=O band at 80 min = 24.3 cm^{-1} , at 160 min = 11.3 cm^{-1} and at 300 min = 2.6 cm^{-1}). Fig. 5c shows the appearance of bands between 1500 and 1640 cm^{-1} . These bands can be ascribed to aromatics C–C stretching vibrations over polyaromatic compounds [33] and/or to vibration of C–O ($\nu_{\text{C-O}}$

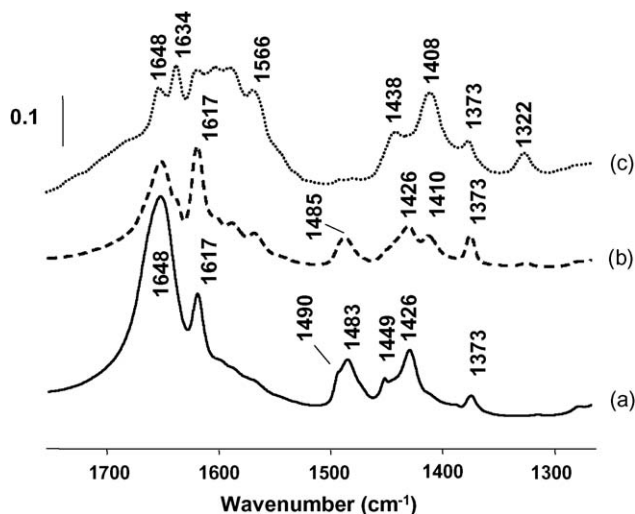


Fig. 5. Spectra of carbonaceous compounds (coke) retained over NaX zeolite during cumene oxidation at 250 °C for various times on stream (80 min (a), 160 min (b) and 300 min (c)).

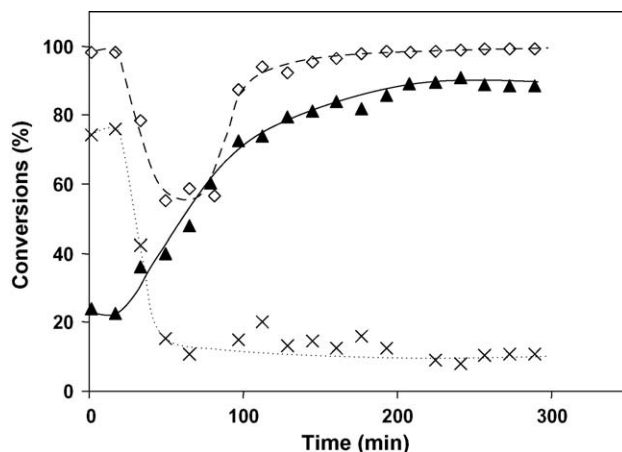


Fig. 6. Catalytic destruction of cumene at 250 °C over NaX pre-activated with acetophenone injection. Cumene conversion (\diamond), CO_2 yield (\blacktriangle) and into coke (\times).

1610–1550 cm^{-1}) due to the presence of oxygenated molecules. It should be noted that the changes in coke nature mostly appear between 160 and 300 min, just after the transitional period. Moreover, the shoulders observed between 1650 and 1750 cm^{-1} especially after 300 min of reaction indicate the presence of other oxygenated compounds than acetophenone.

3.4. Acetophenone effect on catalyst

The determination of one part of the coke (acetophenone) present on the catalyst between 80 and 300 min reaction for cumene oxidation at 250 °C led us to study the effect of oxygenated coke on the reaction behaviour with time-on-stream. 100 min before the beginning of the reaction, 5 μL of acetophenone (this volume being close to the coke amount measured on the catalyst) were introduced in the reactor, under airflow and with a needle, to be adsorbed on a fresh zeolite. Fig. 6 shows the evolution of global cumene conversion and its conversion into CO_2 and into by-products and coke as a function of time at 250 °C and after acetophenone injection. Results revealed similarities between cumene oxidation at 250 °C (Fig. 2) and cumene oxidation after preliminary acetophenone injection (Fig. 6). However, the increase of CO_2 yield with the injection of acetophenone was faster than the increase observed at 250 °C on Fig. 2. Moreover, infrared spectroscopy (Fig. 7) shows the formation of a coke of same nature with or without acetophenone injection. The coke amount measured at the end of the reaction (300 min) was close to 1.9 wt%. Thus, the activation observed for cumene oxidation could be due, in part and at least indirectly, to the formation of acetophenone on NaX. Nevertheless, the conversion of cumene and the CO_2 yield did not started at 100%. This indicates that acetophenone is not the active species but a precursor in the formation of the active species, which should be polyaromatic oxygenated molecules. Indeed, IR study (Fig. 5) in the previous subsection showed the acetophenone disappearance during reaction.

These results led us to estimate the number of sites made inactive by the presence of adsorbed molecules. On the NaX zeolite unit cell, over the 88 Na^+ cations only those in positions II and III are accessible to common organic molecules, which represent a number of 61 accessible Na^+ cations [34]. Thus, if coke is assimilated exclusively to acetophenone, and if it is assumed that one Na^+ cation adsorbs one acetophenone molecule, it is then possible to calculate the number of Na^+ cations virtually occupied

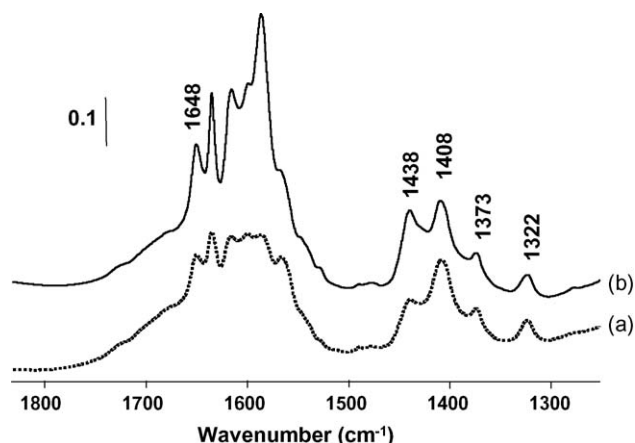
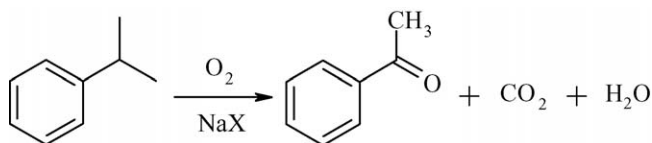


Fig. 7. Spectra of carbonaceous compounds (coke) retained at 150 °C over NaX zeolite during cumene oxidation at 250 °C and 5 h reaction without (a) and with (b) introduction of acetophenone.

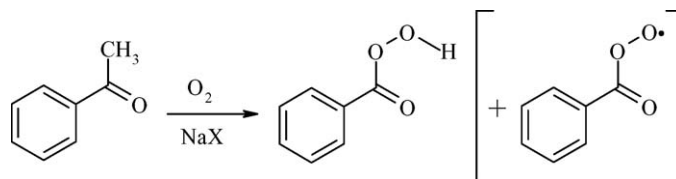
by acetophenone: 3.1 wt% of coke corresponds then to 0.026 mol of acetophenone against 0.45 mol of accessible Na^+ cations in 100 g of zeolite. In that case only 5.7% of the accessible cations are occupied. Even if acetophenone adsorbed on more than one Na^+ cation it would therefore not be possible to neutralize more than 95% of the accessible Na^+ cations as it was the case according to IR experiments. Moreover, as seen before, other molecules like biphenyl and terphenyl were also observed. Taking into account the presence of monoaromatics and polyaromatics molecules in the coke it is possible to estimate the volume of the zeolite occupied by these molecules. As we did not know the relative abundance of all the molecules trapped into the zeolite at the end of the reaction an average density of 1.1 was used ($d_{\text{acetophenone}} = 1.0281 \text{ g mL}^{-1}$, $d_{1,3\text{-diphenyl-2-propen-1-one}} = 1.0712 \text{ g mL}^{-1}$, $d_{\text{m-terphenyl}} = 1.199 \text{ g mL}^{-1}$). Assuming that adsorbed molecules have a similar density than the corresponding liquids, the results showed that in that case less than 10% of the zeolite porous volume would be occupied by coke. These results seem to demonstrate that zeolite porous system is rather hindered than filled by the coke and that acetophenone does not neutralize Na^+ cations by specific adsorption. Thus, we can conclude that coke is essentially present near the aperture of the zeolite cages and blocks the access of pyridine and consequently that of cumene. In this particular case, cumene oxidation seems then to occur near the external surface or at the pore mouth of the catalyst.

3.5. Proposal for cumene oxidation over NaX zeolite

The first step for cumene oxidation would be the formation of acetophenone with a CO_2 and water release (acetophenone adsorbed on the catalyst was detected by IR spectroscopy and by GC/MS after Soxhlet extraction):



The second step could be the transformation of acetophenone into “active coke” molecules, which could be peroxide (or peroxy radical) compounds like those already suggested in liquid phase oxidation of cumene [35–37]:



These peroxides can be stabilized in the zeolite by Na^+ cations, essentially Na^+ cations in position III (four cations per supercages), which can stabilize up to four peroxide molecules. It should be noted that these cations are located near the aperture of the porous system [34], which is in agreement with the pore mouth catalysis previously proposed. Actually, cations in position III acts certainly in the formation/stabilization of these compounds since in our experimental conditions no activation in CO_2 yield was observed over NaY zeolite, which is structurally identical to NaX but does not possess any cation in position III. Moreover, radical stabilizers proved to have an important effect on the formation rate and selectivity towards cumene hydroperoxide [37]. In our case, the presence of compounds similar to the peroxides proposed would be presumed after 300 min reaction according to the $\nu_{\text{C-O}}$ bands in the 1550–1650 cm^{-1} range and at 1408 cm^{-1} (Fig. 5c). Peroxides can then act as oxidants to transform cumene into CO_2 and H_2O and afterwards, peroxides can be regenerated by action of oxygen and reaction can therefore be autocatalytic.

4. Conclusions

The oxidation of cumene was studied under experimental conditions close to the industrial specifications (humid air, 18000 h^{-1} GHSV). An interesting activation phenomenon was observed on the conversion of cumene and its conversion into CO_2 on NaX catalyst at 250 and 280 °C. This particular experimental fact is not related to a modification of the zeolite or to a coke combustion during the reaction time but seems to result from the formation of oxygenated organic species usually known as “active coke” able to catalyze oxidation reactions. The study of coke showed the presence of oxygenated aromatics and polyaromatics compounds. Among these compounds we can mention the particular presence of acetophenone. Results obtained showed that the introduction of acetophenone in the NaX zeolite before reaction increased its oxidative power. However, acetophenone seems not to be the specie promoting oxidation but probably a reaction intermediate for the formation of the active compounds, which would be peroxides or peroxy radicals. Finally, these active compounds seem to be located near the apertures of the catalyst porous system leading to a pore mouth catalysis process.

Acknowledgments

We thank C. Canaff for the GC–MS experiments and J.-D. Comparot for the IR characterizations. R. Beauchet gratefully acknowledges the “Agence de l’environnement et de la Maîtrise de l’énergie” (ADEME) and the Région Poitou-Charentes for his Ph.D. grant.

References

- [1] J. Spivey, Ind. Eng. Chem. Res. 26 (1987) 2165–2180.
- [2] F. Bertinchamps, C. Grégoire, E.M. Gaigneaux, Appl. Catal. B 66 (2006) 1–9.
- [3] R. López-Fonseca, A. Aranzabal, J.I. Gutiérrez-Ortiz, J.I. Álvarez-Uriarte, J.R. González-Velasco, Appl. Catal. B 30 (2001) 303–313.
- [4] R. López-Fonseca, B. de Rivas, J.I. Gutiérrez-Ortiz, A. Aranzabal, J.R. González-Velasco, Appl. Catal. B 41 (2003) 31–42.
- [5] R. López-Fonseca, J.I. Gutiérrez, J.L. Ayastui, M.A. Gutiérrez-Ortiz, J.R. González-Velasco, Appl. Catal. B 45 (2003) 13–21.
- [6] R. López-Fonseca, J.I. Gutiérrez, J.R. González-Velasco, Catal. Commun. 5 (2004) 391–396.

- [7] E. Finocchio, C. Pistarino, S. Dellepiane, B. Serra, S. Braggio, M. Baldi, G. Busca, *Catal. Today* 75 (2002) 263–267.
- [8] R. López-Fonseca, J.I. Gutiérrez, J.R. González-Velasco, *Appl. Catal. A* 271 (2004) 39–46.
- [9] H. Figueiredo, I.C. Neves, C. Quintelas, T. Tavares, M. Taralunga, J. Mijoin, P. Magnoux, *Appl. Catal. B* 66 (2006) 274–280.
- [10] J. Tsou, P. Magnoux, M. Guisnet, J.J.M. Órfão, J.L. Figueiredo, *J. Catal.* 225 (2004) 147–154.
- [11] J. Tsou, P. Magnoux, M. Guisnet, J.J.M. Órfão, J.L. Figueiredo, *Appl. Catal. B* 51 (2004) 129–133.
- [12] L. Pinard, P. Magnoux, P. Ayrault, M. Guisnet, *J. Catal.* 221 (2004) 662–665.
- [13] L. Pinard, J. Mijoin, P. Ayrault, C. Canaff, P. Magnoux, *Appl. Catal. B* 51 (2004) 1–8.
- [14] M. Taralunga, J. Mijoin, P. Magnoux, *Catal. Commun.* 7 (2006) 115–121.
- [15] R. Beauchet, P. Magnoux, J. Mijoin, *Catal. Today* 124 (2007) 118–123.
- [16] J. Tsou, P. Magnoux, M. Guisnet, J.J.M. Órfão, J.L. Figueiredo, *Appl. Catal. B* 57 (2005) 117–123.
- [17] N. Burgos, M. Paulis, M. Mirari Antxustegi, M. Montes, *Appl. Catal. B* 38 (2002) 251–258.
- [18] P. Papaefthimiou, T. Ioannides, X.E. Verykios, *Appl. Catal. B* 13 (1997) 175–184.
- [19] R.W. van den Brink, P. Mulder, R. Louw, *Catal. Today* 54 (1999) 101–106.
- [20] R.W. van den Brink, P. Mulder, R. Louw, *Appl. Catal. B* 25 (2000) 229–237.
- [21] M. Taralunga, B. Innocent, J. Mijoin, P. Magnoux, *Appl. Catal. B* 75 (2007) 139–146.
- [22] M. Guillelot, J. Mijoin, S. Mignard, P. Magnoux, *Appl. Catal. A* 327 (2007) 211–217.
- [23] A. Galdino Figueira de Souza, A.M. Portilho Bentes Jr., A.C. Camacho Rodrigues, L.E. Pizarro Borges, J.L. Fontes Monteiro, *Catal. Today* 107–108 (2005) 493–499.
- [24] R. Rachapudi, P.S. Chintawar, H.L. Greene, *J. Catal.* 185 (1999) 58–72.
- [25] M. Guisnet, P. Ayrault, J. Datka, *Pol. J. Chem.* 71 (1997) 1455–1461.
- [26] J.W. Ward, in: J.A. Rabo (Ed.), *Zeolite Chemistry and Catalysis*, ACS Monograph 171, American Chemical Society, Washington DC, 1976, p. 226.
- [27] J.R. Sohn, S.I. Decanio, J.H. Lunsford, D.J. O'Donelle, *Zeolites* 6 (1986) 225–227.
- [28] M. Flanigen, in: J. Rabo (Ed.), *Zeolite Chemistry and Catalysis*, ACS Monograph, 171, American Chemical Society, Washington, DC, 1976, p. 80.
- [29] F. Thibault-Starzyk, *Les Matériaux Micro et Mesoporeux – Caractérisation*, EDP Sciences, Les Ulis, 2004, p. 59.
- [30] M. Guisnet, P. Magnoux, *Appl. Catal. A* 54 (1989) 1–27.
- [31] J.D. Lee, N.-K. Park, S.O. Ryu, K. Kim, T.J. Lee, *Appl. Catal. A* 275 (2004) 79–86.
- [32] P. Magnoux, H.S. Cerqueira, M. Guisnet, *Appl. Catal. A* 235 (2002) 93–99.
- [33] G. Caeiro, P. Magnoux, J.M. Lopes, F. Ramôa Ribeiro, *Appl. Catal. A* 292 (2005) 189–199.
- [34] D.H. Olson, *Zeolites* 15 (1995) 439–443.
- [35] G. Sereda, V. Rajpara, *Tetrahedron Lett.* 48 (2007) 3417–3421.
- [36] M.V. Tsodikov, V.Ya. Kugel, E.V. Slivinskii, G.N. Bondarenko, Yu.V. Maksimov, M.A. Alvarez, M.C. Hidalgo, J.A. Navio, *Appl. Catal. A* 193 (2000) 237–242.
- [37] S. Matsui, F. Fujita, *Catal. Today* 71 (2001) 145–152.